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13. ABSTRACT (Maximum 200 Words) Methods developed and refined to characterize ion and molecular transport process in disordered media are described. The primary tool is pulsed field gradient NMR. A static field gradient method was developed which makes possible variable pressure diffusion measurements, and the application to the important fuel cell membrane NAFION constitute the first results of their kind ever published. Standard ambient pressure results for lithium ion conducting polymer electrolytes containing nanoscopic silica are included, as well as the description of a novel scheme to produce highly conducting polymer electrolytes by magnetic field alignment of the polymer chains. Fuel cell membranes developed by collaborators at Wright-Patterson Air Force Base were also investigated.				
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Technical Objectives

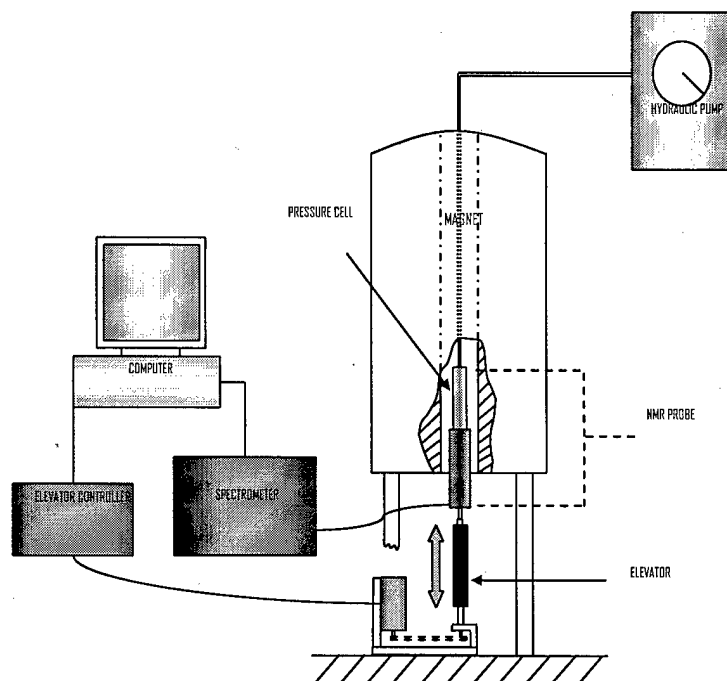
Promising strategies for development of direct methanol fuel cells are being pursued by our colleagues at the U.S. Naval Academy, Tel Aviv University, the University of Rome, and Wright-Patterson Air Force Base as well other collaborators. Our objective is to provide atomic/molecular level characterization of structure and transport in proton-conducting membrane and catalyst materials in order to provide a better understanding of electrochemical behavior and performance limitations of the samples provided by our colleagues.

Technical Approach

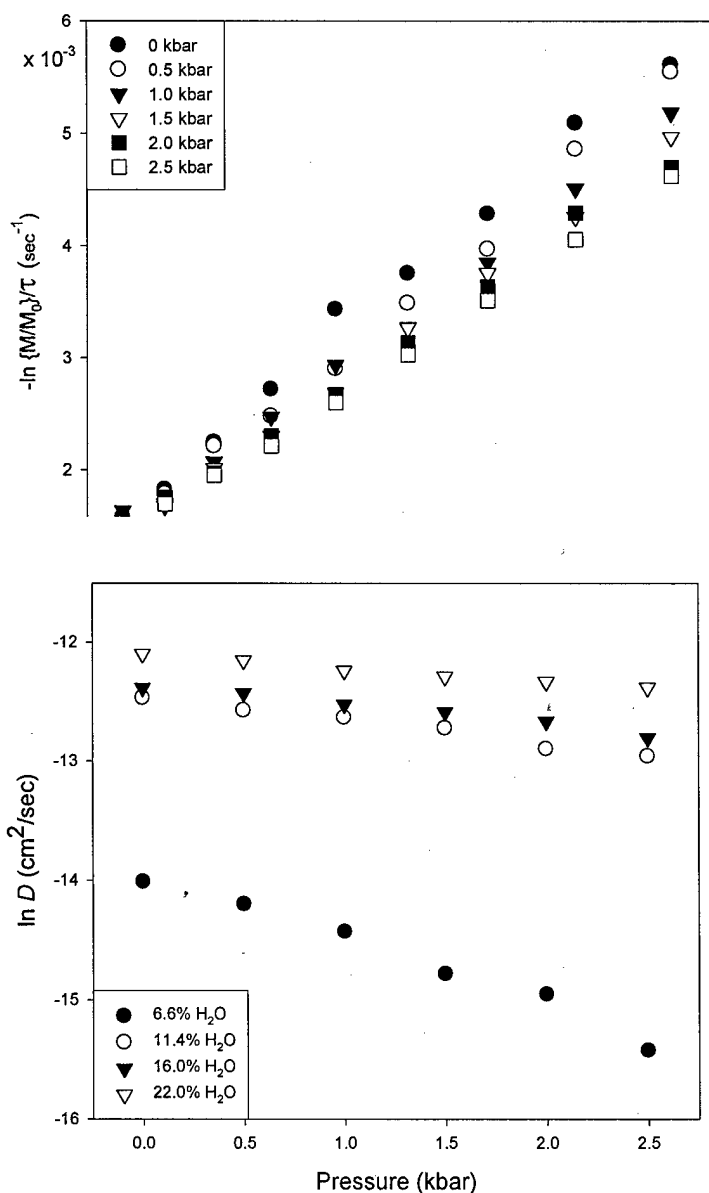
Nuclear magnetic resonance (NMR) is utilized to characterize water and methanol molecular mobility and host polymer - solute interactions. Self-diffusion coefficients of both water and methanol (or other liquid fuels) in polymer electrolyte membranes equilibrated in water/methanol solution are determined by pulsed field gradient techniques. The relationship between the diffusion results, which reflect macroscopic charge and mass transport, and spin-lattice relaxation measurements, which are sensitive to nm-scale motional processes is examined in order to shed light on the proton transport mechanism. X-ray absorption spectroscopy (EXAFS and NEXAFS) is utilized to characterize local structure of various catalyst compositions sputtered directly onto electrolyte membranes.

Progress

With partial AFOSR funding, we have developed an NMR system to measure self-diffusion coefficients at higher pressures because of two timely developments: (i) the replacement of the stainless steel (which is slightly magnetic at 7 T fields) pressure bomb with a Cu/Be high pressure alloy; (ii) accumulated experience in measuring self-diffusion in *static* field gradients, i.e. in the fringe field of the NMR magnet. A schematic of the set-up is shown below.



Self-diffusion measurements using *static* field gradients, while technically more difficult than “standard” PFG measurements, offer two important advantages. The first is that the static gradient strengths are typically an order of magnitude greater than pulsed gradients, which will permit measurements of order-of-magnitude lower diffusion coefficients than accessible by PFG methods. This will then make possible the extension of diffusion measurements in polymer electrolytes and polymer nanocomposites down to lower temperatures than current capabilities allow. The second advantage is that, in combination with our high pressure NMR probe, it will be possible to measure self-diffusion coefficients in polymer electrolytes as a function of hydrostatic pressure. As proof-of-principle, we have obtained the first documented (to our knowledge) pressure-dependent diffusion data in a membrane, or for that matter, any composite system (not a pure element or compound). Shown below are echo decay data used to determine the self diffusion coefficient for a typical hydrated Nafion sample. The second figure displays the diffusion coefficients in Nafion as a function of water content, which in turn can be used to calculate the activation volumes. We expect the high-pressure diffusion measurements to lead to significant new insights into the conduction mechanisms of polymer electrolytes.

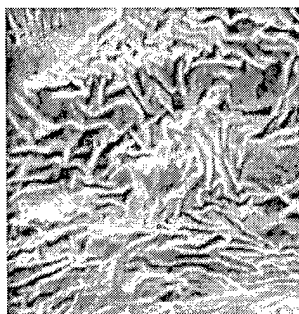


In collaboration with Dr. Robert Mantz at WPAFB, we have investigated a series of highly sulfonated polyarylenethioethersulfone (SPTES) polymer membranes developed at WPAFB. The ^1H spectra as well as the diffusion rates were determined as a function of temperature. Comparison of conductivity and diffusion activation energies indicate that H^+ and water transport are closely correlated. These membranes were also examined for possible application in direct methanol fuel cells, by measuring both water and methanol diffusion in samples equilibrated in 2M methanol solution. The results indicate that methanol mobility is lower, relative to water mobility in SPTES membranes than in NAFION.

In collaboration with Dr. Stefano Passerini of ENEA (the Italian National Energy Laboratory), we have shown that PEO/BETI complexes prepared with fumed silica show only a small difference in conductivity and ionic diffusivity compared to silica-free materials. The significance of this controversial result is that the polymer electrolytes were prepared by a solvent-free, hot-pressing method, suggesting that the widely observed nanoparticle enhancement of conductivity could be associated at least to some extent with solvent retention by the nanoparticles. Obviously a better understanding of these issues is central to the development of new, stable power sources for military applications. The most important civilian application concerns economically feasible batteries for electric vehicles.

In collaboration with J. Fontanella (US Naval Academy) and Gary Wnek (Virginia Commonwealth Univ.) we have used standard pulsed field gradient NMR results to show that the water and ion transport properties in electrosprayed NAFION are essentially the same as in commercial films.

In collaboration with E. Peled, (Tel Aviv Univ.), we have developed a means for orienting polymer electrolytes perpendicular to the casting plane by using a strong inhomogeneous magnetic field. Prior work by our groups (also partly funded by NMR) demonstrated significant conductivity enhancement in mechanically oriented (i.e. stretched) polymer electrolyte films. The current work is far more relevant to applications because the conductivity enhancement is in the technologically useful direction (perpendicular to the plane). Evidence of orientation in the field from electron microscopy is shown below.



x2000

a



x2000

b

X-sectional electron micrographs of random (a) and magnetically oriented (b) polymer electrolyte based on PEO

Personnel Supported

Most of the personnel listed have received only partial AFOSR support. The remainder comes from ONR, and DoE grants.

PI: Steve Greenbaum

Visiting Professors: Stan Bajue and John Flowers, Medgar Evers College of CUNY (part-time),

Postdoc: Jay Jayakody

Doctoral Students: Sophia Suarez, and Eugene Mananga. Sophia Suarez successfully defended her thesis in December 2003 and is now an NRC postdoc at NRL.

MA Students: Dan Carter, Nicole Leifer; degree completion for both is scheduled for June 2004.

Three undergraduate research students are also involved with the project; most of their funds come from NIH's Minority Access to Research Careers Program.

Recent Publications (related to this effort but also funded by other programs in addition to AFOSR)

124. "A Solid-State ^{51}V NMR Characterization of Vanadium Sites in $\text{LiCo}_x\text{Ni}_{1-x}\text{VO}_4$, with P.E. Stallworth, X. Guo, E. Tatham, M. Arrabito, and N. Penazzi, *Solid State Ionics*, 170, 181 (2004).
125. "X-ray diffraction and ^7Li nuclear magnetic resonance studies of iron and cobalt substituted LiNiO_2 prepared from inorganic transition metal nitrates", with X. Guo, F. Ronci, and B. Scrosati, *Solid State Ionics*, 168 pp. 37-49 (2004).
126. "High Pressure NMR Study of Water Self-Diffusion in NAFION-117 Membrane", with J. R.P. Jayakody, P.E. Stallworth, E. Mananga, J. Zapata-Farrington, *Journal of Physical Chemistry B* 108, 4260 (2004).
127. "X-ray Absorption Spectroscopy Investigation of the Sub-Nanoscale Strain in Thin-Film Lithium Ion Battery Cathodes", with F. Alamgir, J. VanSluytman, D. Carter, J. Whitacre, C.-C. Kao, and M. denBoer, *Materials Research Society Symposium Proceedings*, , vol .822, S2.3.1 (2004).
128. "New Generation Of Ordered Polymer Electrolytes For Lithium Batteries", with D. Golodnitsky, E. Livshits, R. Kovarsky, E. Peled, S. Chung, and S. Suarez, *Electrochemical and Solid State Letters*, in press.
129. "Solid State NMR Studies of Lithium Phosphorus Oxynitride Films Prepared by Nitrogen Ion Beam-Assisted Deposition", with P.E. Stallworth, F. Vereda, T.E. Haas, P. Zerigian, and R. Goldner, *Journal of the Electrochemical Society*, in press.
130. "A New Class of Lithium Hybrid Gel Electrolyte (HE) Systems", with M. Vittadello, S. Suarez, K. Kano, V. Di Noto, and T. Furukawa, *Journal of Physical Chemistry*, in press.
131. " LiCoO_2 thin-film batteries: Structural changes and charge compensation", with

F.M. Alamgir, E. Strauss, J.F. Whitacre, M. Denboer, S. Neih, And C.-C. Kao, *Journal Of The Electrochemical Society*, In Press

132. "The Effect of Electrolyte Type upon the High Temperature Resilience of Lithium Ion Cells", with M. C. Smart, B. V. Ratnakumar, J. Whitacre, L. Whitcanack, K. Chin, M. Rodriguez, D. Zhao, and S. Surampudi, *Journal of the Electrochemical Society*, in press.
 133. "High Field ^7Li and ^{19}F MAS NMR identification of LiF in the SEI Layer in Lithium Ion Battery Electrodes", with B.M. Meyer, N.D. Leifer, S. Sakamoto, and C.P. Grey, *Electrochemical and Solid State Letters*, submitted.
 134. "A Lithium Z-Iope Based on PEG600, $(\text{CH}_3)_2\text{SnCl}_2$, and $\text{Li}_3\text{Fe}(\text{CN})_6$ ", with M. Vittadello, S. Gustave, K. Fujimoto, V. Di Noto, and T. Furukawa, *Journal of the Electrochemical Society*, in press.
 135. "NMR Studies of Mass Transport in Lithium Conducting Polymer Electrolytes", with Sophia Suarez, J.R. P. Jayakody, Eugene S. Mananga, and Song-Ho Chung, San Antonio ECS Proceedings, in press.
 136. Investigation Of Highly Sulfonated Polyarylenethioethersulfones For Fuel Cell Applications, with J.R.P. Jayakody, Ameesh. Khalfan, Thuy D. Dang, Zongwu Bai, and Robert A. Mantz, Electrochemical Society Proceedings on Polymer Electrolyte Membranes, X2, Fall 2004.
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